

5.2. CONTINUING PROGRAMS

5.2.1. FLASK SAMPLES

Overview

Arrangements were made in 2001 to add two new stations to the sampling network. One of these is an additional remote site in the far southern hemisphere, located at Ushuaia, near Tierra del Fuego (TDF), Argentina (Figure 5.1, Table 5.1). This is a cooperative site with the Argentine government and is a Global Atmospheric Watch (GAW) station sponsored by the World Meteorological Organization (WMO). The second site, located at Trinidad Head, California (THD), is considered a regional sampling site and has been established for evaluating regional-scale air quality. It is anticipated that Trinidad Head will receive a mix of air from over the remote ocean and from nearby forests and small towns. It also may be useful for detecting air masses transported from Asia. Sampling at Mace Head, Ireland (MHD), was suspended for almost a year, as flasks began disappearing in transit. Biweekly sampling at MHD was reinitiated near the end of 2001. Efforts to improve sampling frequency and precision at all sites have continued throughout 2000-2001.

Flasks brought into the laboratory are analyzed on two to four instruments, depending upon the species being examined and the size of the individual sampling flask (Table 5.2). Analyses are performed by a gas chromatograph with electron capture detection (GC-ECD) and/or a gas chromatograph with mass spectrometric (GC-MS) detection. Although all 300-ml flasks have been retired, there still remain some 850-ml flasks, which contain a marginal amount of air for all of these low-level analyses. Most flask analyses are of samples from the network, although many are from research cruises, firm air sampling, and other special projects. One hundred new electro-polished, stainless-steel flasks were recently purchased

from Lab Commerce (formerly known as Meritor Corporation, San Jose, California) to supply the new sites, to upgrade flask quality and quantity at old sites, and to use for special projects.

In 1996, 269 flasks from the network were filled and delivered to the Boulder laboratory for analysis. This number has increased each year, reaching a total of 415 in 2000 (Figure 5.2). This increase is the result of added sites and more efficient turnover of flasks between Boulder and the field sites. This was accomplished through improved record keeping of flasks coming to Boulder and by addition of flasks to the network. Sampling success has steadily improved from that for 1996 at all sites (Table 5.3). This was mainly the result of small leak repairs and valve replacements on flasks, where necessary. These repairs greatly improved the agreement in flask pressure between simultaneously sampled pairs (Figure 5.3).

GC-ECD Results

CFC-12 continues to increase in the atmosphere; however, it may have leveled off in the northern hemisphere (Figure 5.4). Mixing ratios of CFC-11 continue to drop steadily (Figure 5.5). The CFC-11 growth rate (-1.75 ± 0.11 (95% C.L.) ppt yr⁻¹, 0.7% yr⁻¹) for 2000 through mid-2001 does not differ from the rate determined for 1997-2001 (-1.73 ± 0.03 ppt yr⁻¹). CFC-113 and CCl₄ are also both decreasing, at about 1% yr⁻¹. The global growth rate of N₂O (Figure 5.6) during 1978-2000 was 0.74 ± 0.01 ppb yr⁻¹, which amounts to a mean of about 0.25% yr⁻¹. During 1999 through mid-2001, the global growth rate was 0.73 ± 0.06 ppb yr⁻¹, which does not differ from the 23-yr average. Sulfur hexafluoride (Figure 5.7) still appears to be increasing linearly in the atmosphere, with a growth rate of about 0.22 ± 0.01 ppt yr⁻¹ since 1996.

The mixing ratios of halons are still increasing slowly in the atmosphere, in spite of a ban on their production in developed countries as of 1994. The global growth rate of halon-1301 (Figure 5.8) from 1999 through 2000 (0.06 ± 0.07 ppt yr⁻¹) does not differ significantly at the 95% confidence level from the 1995-2000 average of 0.06 ± 0.01 ppt yr⁻¹, nor from the 1995-1996 average of 0.044 ± 0.011 ppt yr⁻¹ reported in Butler et al. [1998]. The growth rate of halon-1211 (Figure 5.9) seems to be slowing, having

TABLE 5.2. Instrumentation for HATS
Flask Analysis

Instrument	Type	Gases	Frequency of Network Data
OTTO	GC-ECD (three-channel, isothermal)	N ₂ O, CFCs (3), CCs (2), SF ₆	Weekly
LEAPS	GC-ECD (one-channel, temperature- programmed)	Halons (2), CH ₃ Cl, CH ₃ Br, CHCl ₃	Semimonthly to monthly
HCFC-MS	GC-MSD (one -channel temperature- programmed)	HCFCs (3), HFCs (1), CFCs (3), halons (1), CCs (6), BrCs (3), COS	Semimonthly
HFC-MS	GC-MSD (one -channel, temperature- programmed)	HCFCs (5), HFCs (2), CFCs (2), halons (2), CCs (6), BrCs (3), BrCCs (3)	Semimonthly to monthly

OTTO, not an acronym; LEAPS, Low Electron Attachment Potential Species; BrCs, bromocarbons; BrCCs, bromochlorocarbons.

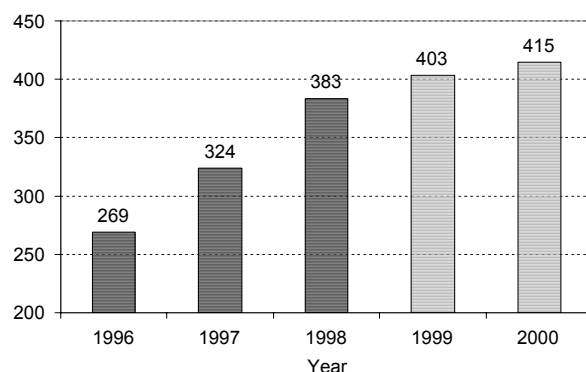


Fig. 5.2. Number of flask pairs filled and returned to Boulder each year from the HATS station network.

TABLE 5.3. Percentage Sampling Success at CMDL Observatories and Cooperative Sampling Sites

Sampling Station	1996	1997	1998	1999	2000
Barrow, AK	69%	94%	88%	87%	90%
Mauna Loa, HI	69%	83%	90%	96%	94%
American Samoa	54%	67%	73%	88%	88%
South Pole	77%	69%	77%	88%	81%
Alert, Canada	52%	46%	67%	67%	65%
Niwot Ridge, CO	63%	92%	87%	77%	88%
Cape Grim, Australia	60%	69%	85%	87%	85%
WLEF tower, WI	12%	35%	69%	92%	100%
Harvard Forest, MA	46%	62%	69%	69%	88%
Kumukahi, HI	50%	54%	67%	69%	83%
Palmer, Antarctica	—	8%	65%	81%	96%
Mace Head, Ireland*	—	—	8%	15%	—
WITN tower, NC†	65%	62%	62%	38%	—

Sampling success is defined as the fraction of flasks analyzed relative to the number expected (i.e., one pair per week).

*Sampling was discontinued temporarily in 2000 because of loss of flasks in shipments.

†Site was discontinued indefinitely in 1999.

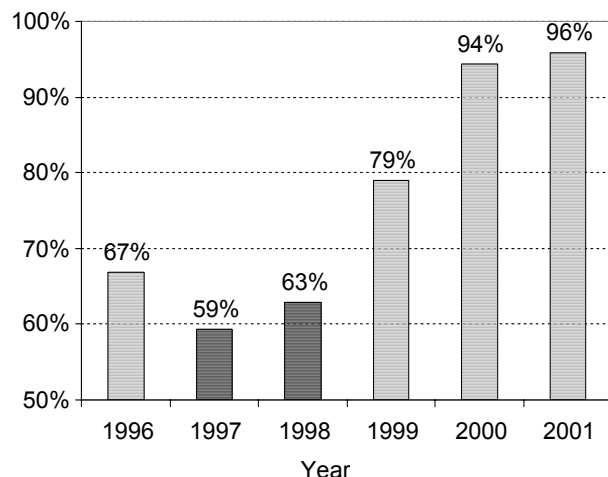


Fig. 5.3. Percentage of flask pairs agreeing within 1 psi in total pressure upon arrival in Boulder.

dropped from a steady rate of 0.16 ± 0.02 ppt yr⁻¹ in the late 1980s and early 1990s to 0.094 ± 0.04 ppt yr⁻¹ for 1999 through mid-2001.

GC-MS Results

Chlorofluorocarbons alternatives measurement program. Measurements of CFC alternatives and other trace gases were continued during 2000-2001 from flasks collected at 12 locations. In both years, three samples per month, on average, were filled and analyzed on GC-MSD instrumentation at 11 of the 12 sites. Fewer samples from MHD were collected and analyzed owing to difficulties associated with shipping.

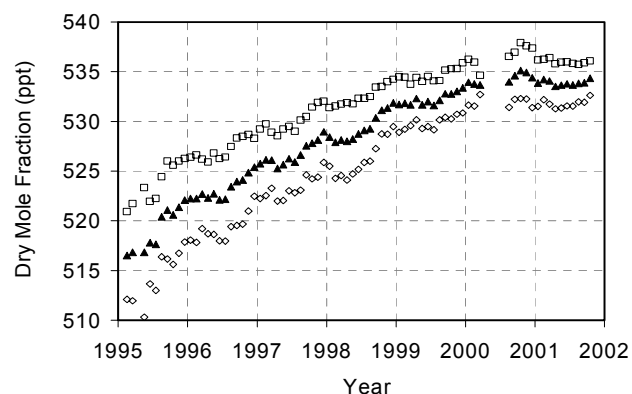


Fig. 5.4. Recent measurements of CFC-12 in the atmosphere. Measurements are monthly averages of GC-ECD data: northern hemisphere means (squares), global means (triangles), and southern hemisphere means (diamonds).

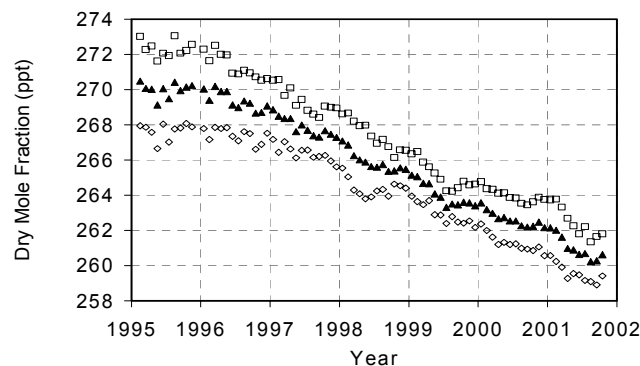


Fig. 5.5. Recent measurements of CFC-11 in the atmosphere showing a steady loss rate since 1997 (GC-ECD monthly means; symbols as in Figure 5.4).

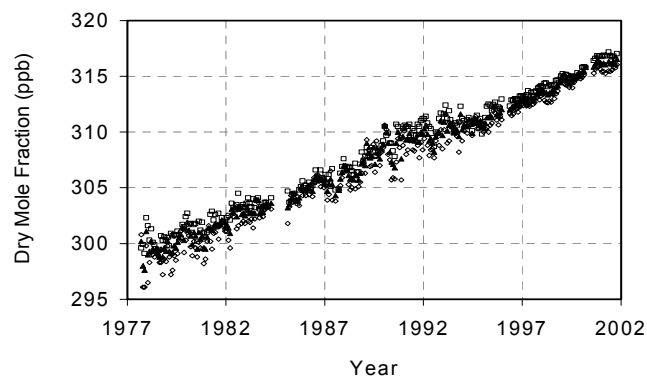


Fig. 5.6. Atmospheric history of N₂O since 1977 (GC-ECD monthly means; symbols as in Figure 5.4). A new GC-ECD instrument has been used since 1994.

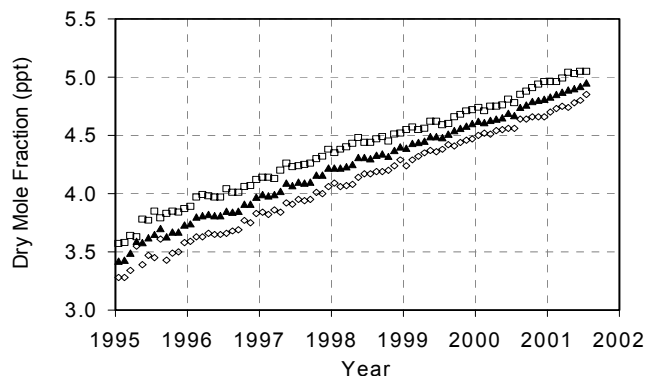


Fig. 5.7. Recent history of atmospheric SF_6 from CMDL flask measurements (GC-ECD monthly means; symbols as in Figure 5.4).

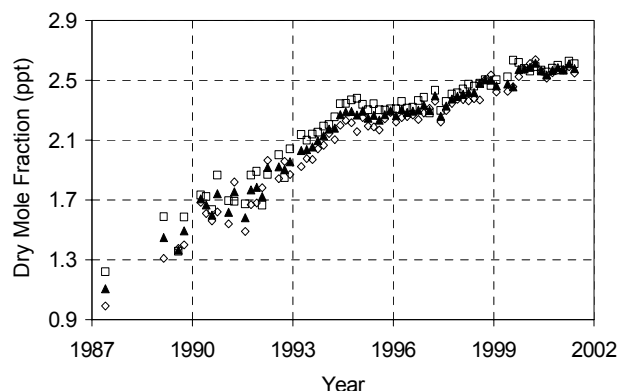


Fig. 5.8. Atmospheric history of halon-1301 (GC-ECD bimonthly averages; symbols as in Figure 5.4).

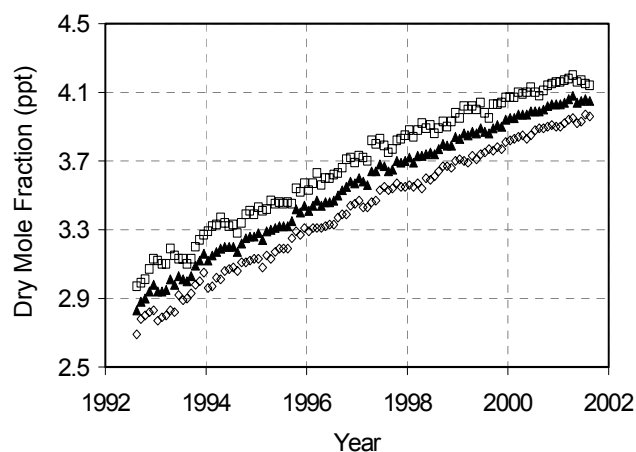


Fig. 5.9. Recent atmospheric history of halon-1211 (GC-MSD monthly means; symbols as in Figure 5.4).

Tropospheric mixing ratios of HCFCs and HFCs continued to increase during 2000-2001 (Figure 5.10, Table 5.4). Fairly linear rates of increase have been observed for HCFC-22, HCFC-141b, HCFC-142b, and HFC-134a since 1998. By mid-2001, chlorine in the three most abundant HCFCs amounted to nearly 190 ppt, or almost 7% of all chlorine carried by long-lived, purely anthropogenic halocarbons. Total chlorine from the HCFCs increased at between 8 and 9 ppt yr^{-1} over this period. Despite rapid

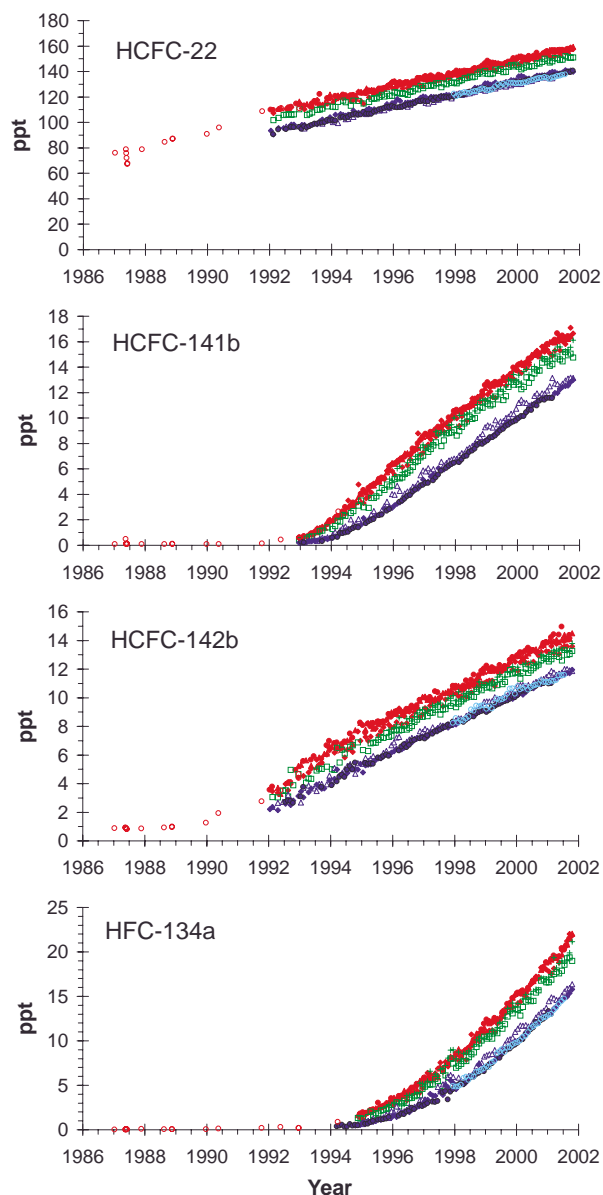


Fig. 5.10. Atmospheric dry mole fractions (ppt) of selected HCFCs and HFC-134a measured by GC-MSD in the CMDL flask program. Each point represents monthly means at one of eight or nine stations: ALT, BRW, NWR, red; KUM, MLO, green; SMO, CGO, PSA, SPO, blue. Also plotted are results from analysis of archived air samples (open red circles) filled at NWR and in past cruises from both hemispheres.

TABLE 5.4. Global Burden (Mixing Ratio) and Rate of Change of HCFCs and HFC-134a

Compound	Mean 2000 (ppt)	Mean 2001 (ppt)	Growth Rate (ppt yr ⁻¹)
HCFC-22	141.6	146.3	5.0 (1992-2001)
HCFC-141b	12.7	14.0	1.7 (1998-2001)*
HCFC-142b	11.7	12.5	1.0 (1998-2001)*
HFC-134a	13.8	17.2	3.2 (1998-2001)

Quantities are estimated from latitudinally weighted measurements at seven remote stations: SPO, CGO, SMO, MLO, NWR, BRW, and ALT.

* Slower growth is indicated in 2000-2001 (0.1-0.2 ppt yr⁻¹ less than shown).

relative growth observed for HFC-134a during the mid-1990s, a fairly constant rate of increase of 3.2 ppt yr⁻¹ has been observed since 1998 (Table 5.4).

Atmospheric methyl chloroform. Atmospheric mixing ratios of methyl chloroform (1,1,1-trichloroethane, CH₃CCl₃) continue to decline exponentially (Figure 5.11). During 2000 through mid-2001, the growth rate of CH₃CCl₃ declined at about 18% yr⁻¹. The exponential decay time constant has been consistent at 5.5 ± 0.1 yr since the beginning of 1998, and continues to provide an upper limit to the global lifetime of CH₃CCl₃ in the atmosphere [Montzka *et al.*, 2000]. If it is presumed those emissions of CH₃CCl₃ have not changed substantially from that estimated for 1998-1999 [Montzka *et al.*, 2000; Prinn *et al.*, 2001], then these results continue to suggest a global lifetime for CH₃CCl₃ of 5.2 years (for the years 1998-2001). In contrast to estimates of CH₃CCl₃ lifetime for the years before 1995, this lifetime estimate is very insensitive to calibration uncertainties. It is still sensitive, however, to the magnitude of present-day emissions.

Slightly shorter estimates of methyl chloroform lifetime have been reported by Prinn *et al.* [2001] for the period 1978-2000. They suggest, however, that the methyl chloroform lifetime has changed over time. They also estimate a lifetime longer than 5.0 years in the later 1990s, which is reasonably consistent with 5.2 years in 1998-2001. The outstanding question with regard to this issue is understanding this apparent change in lifetime. Does it stem from inaccurate estimates of emissions, decreases in OH in recent years, or a change in the true lifetime of methyl chloroform that is unrelated to OH?

The hemispheric difference has not changed substantially since 1998; for the years 1998-2001, the hemispheric difference is estimated to be 2.8 (±0.4)%. This difference is similar at all sampling stations at comparable latitudes in the two hemispheres: 2-3% in the tropics deduced from SMO, MLO, and KUM data; 2-3% in midlatitudes deduced from CGO, NWR, and LEF data; and 2-4% in polar regions deduced from PSA, SPO, BRW, and ALT data (see Table 5.1 for station definitions and locations). The constancy in both the decay time constant and the hemispheric difference suggests that the influence of emissions on estimates of global lifetime and hemispheric lifetimes has either been small or relatively constant since 1998.

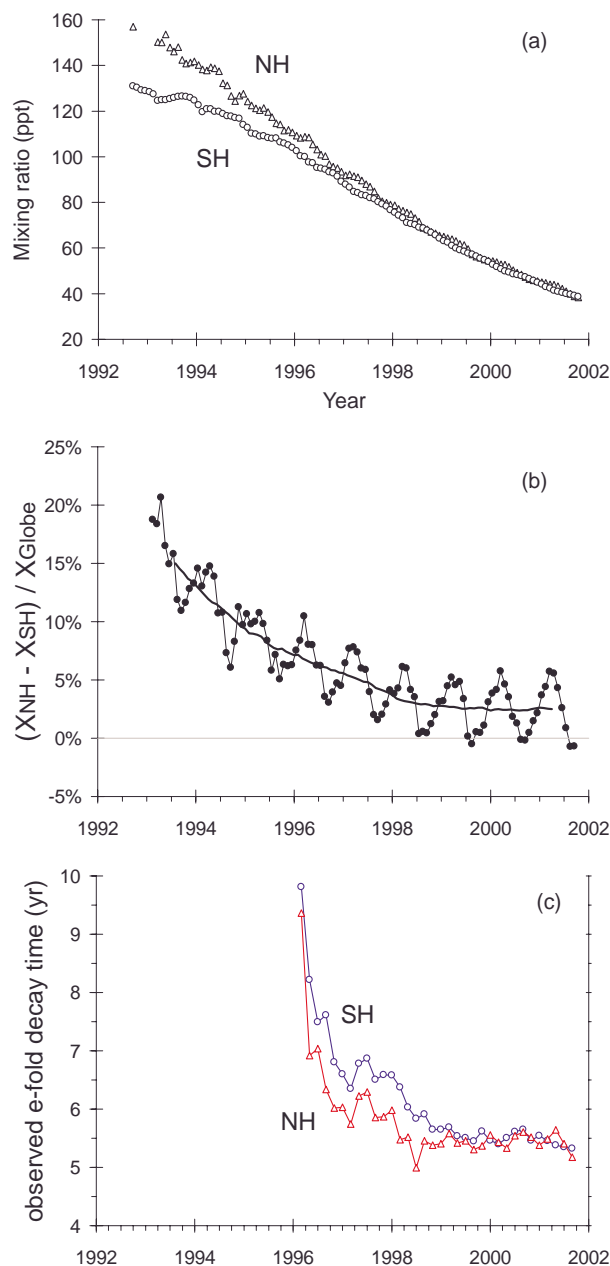


Fig. 5.11. (a) Atmospheric dry mole fractions (ppt) of CH₃CCl₃ measured by GC-MSD in the CMDL flask program. Each point represents a monthly hemispheric surface mean as determined by a latitudinal weighting of results from individual sampling stations (northern hemisphere = triangles, southern hemisphere = circles). (b) The hemispheric mixing ratio difference for CH₃CCl₃ at the Earth's surface in recent years. The difference was inferred from weighted, monthly mean mixing ratios at three to six sampling stations in each hemisphere. Monthly differences (solid circles) are connected with a thin line; the heavy curve represents a 12-mo running mean difference. (c) The observed e-fold decay time for monthly hemispheric surface means of CH₃CCl₃ shown in (a). A fairly constant exponential decay in surface mixing ratios of CH₃CCl₃ has been observed since the beginning of 1998; the exponential time constant for this decay is 5.5 years.

Overall trends in ozone-depleting gases. Ground-based measurements provide an indication of the burden and trend of individual ozone-depleting gases. The sum of chlorine and bromine atoms in long-lived trace gases provides an estimate of equivalent tropospheric chlorine (ETCl) after the enhanced efficiency of bromine to destroy ozone compared with chlorine is included (a factor of 50 is used here; *Solomon et al.* [1995]). ETCl provides an indication of the upper limit to ozone-depleting chlorine and bromine in the future stratosphere. Better approximations of trends in inorganic halogen in the lower stratosphere can be derived from ETCl after accounting for the different rates at which halocarbons photo-oxidize in the stratosphere. These rates have been estimated empirically or with models and are applied as weighting factors to mixing ratios of individual gases in the calculation of effective equivalent chlorine (EECl) and effective equivalent stratospheric chlorine (EESC) [*Daniel et al.*, 1995; *Montzka et al.*, 1996]. The only difference between EECl and EESC is that EESC explicitly includes a 3-yr time lag (dates associated with EECl correspond to the time when the surface measurement was made).

The net sum of ozone-depleting halogen from purely anthropogenic gases continued to decrease during 2000-2001 (Figure 5.12). The rates of decline for EECl and ETCl in 2001 were about 1% yr⁻¹ and 0.5% yr⁻¹, respectively. Amounts of EECl during mid-2001 were about 5.5% below the peak observed near the beginning of 1994. The rate of decline in both EECl and ETCl has slowed by about one-third compared with peak values as the influence of methyl chloroform has diminished.

The two scenarios for EECl and ETCl shown in Figure 5.12 provide some insight into causes of past changes and the future evolution of net halogen in the atmosphere. The measured trends in EECl and ETCl since 1998 have remained fairly close to scenario A, in which constant emissions were presumed [*Montzka et al.*, 1999]. Although substantial reductions in emissions were realized during the 1990s, these results suggest that these emission reductions have slowed in recent years, perhaps owing to enhanced CFC production in developing countries.

The updated projections for scenario B (Figure 5.12, solid lines) are somewhat different from the ones made previously (see references noted in Figure 5.12). The main difference arises from consideration of halons in the future. In the present calculation it has been assumed halon emissions will decrease in future years in reasonable accord with reported halon production [*Fraser et al.*, 1999] and a small allotment for additional future production.

Shorter-lived gases. Measurements of other chlorinated and brominated trace gases were continued during 2000-2001 (Figure 5.13). The results suggest further decreases in mixing ratios of CH₂Cl₂ and C₂Cl₄. Interannual variability is observed for the methyl halides and will be discussed in future publications.

Non-stainless-steel flasks circulated to sampling stations. Although most samples are routinely collected in stainless-steel flasks in the HATS program, glass flasks have also been used recently. Glass flasks are particularly useful when known artifacts affect sampling in steel flasks. Glass flasks sampled during the South Pole 2000 winter allowed for additional measurements of compounds that undergo

substantial degradation in stainless-steel flasks during the long period between sampling and analysis (Figure 5.14). Glass flasks are also useful to determine if results for more reactive gases are independent of flask type. Preliminary results of glass flasks filled at CGO and SPO show good consistency for HCFC-22, HCFC-142b, and HFC-134a. Glass flasks are not without problems for some compounds, however. Poor consistency is observed for HCFC-141b and C₂Cl₄ in glass flasks; this contamination probably is associated with the Teflon seals in these flasks and does not suggest trouble in results reported from stainless-steel flasks for these gases.

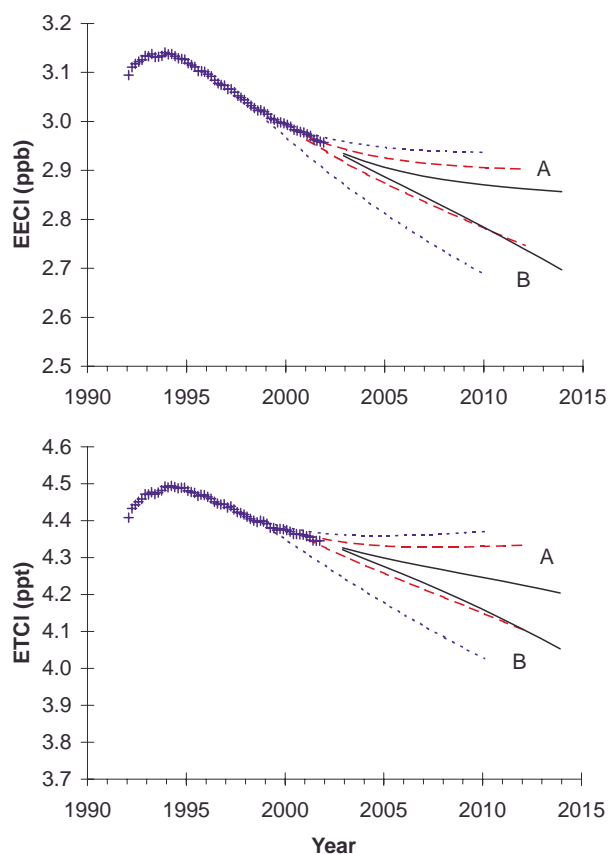


Fig. 5.12. The measured and potential future burden of ozone-depleting halogen in the lower atmosphere. Ozone-depleting halogen is estimated from tropospheric measurements of anthropogenic halocarbons by appropriate weighting factors to calculate effective equivalent chlorine (EECl) for midlatitudes (top) and equivalent tropospheric chlorine (ETCl) as an upper limit for polar latitudes (bottom) [*Daniel et al.*, 1995; *Montzka et al.*, 1996, 1999]. A constant offset was added to account for CH₃Cl and CH₃Br. Projections are based on two limiting scenarios: A, emissions of all long-lived halogenated gases (CFCs, HCFCs, CH₃CCl₃, CCl₄, and halons) remain constant at 2001 levels, and B, scenario A with the exception that emissions of CFCs, CH₃CCl₃, halons, and CCl₄ continue decreasing at 5 to 8% yr⁻¹. Future scenarios have been formulated in previous *CMDL Summary Reports* and other publications with ambient air measurements through 1997 (short-dashed lines [*Daniel et al.*, 1995]) and through 1999 (long-dashed lines [*Hall et al.*, 2001]). Updates to current emission rates and their rates of change based on measurements through 2001 were used to update projections for both scenarios (solid lines).

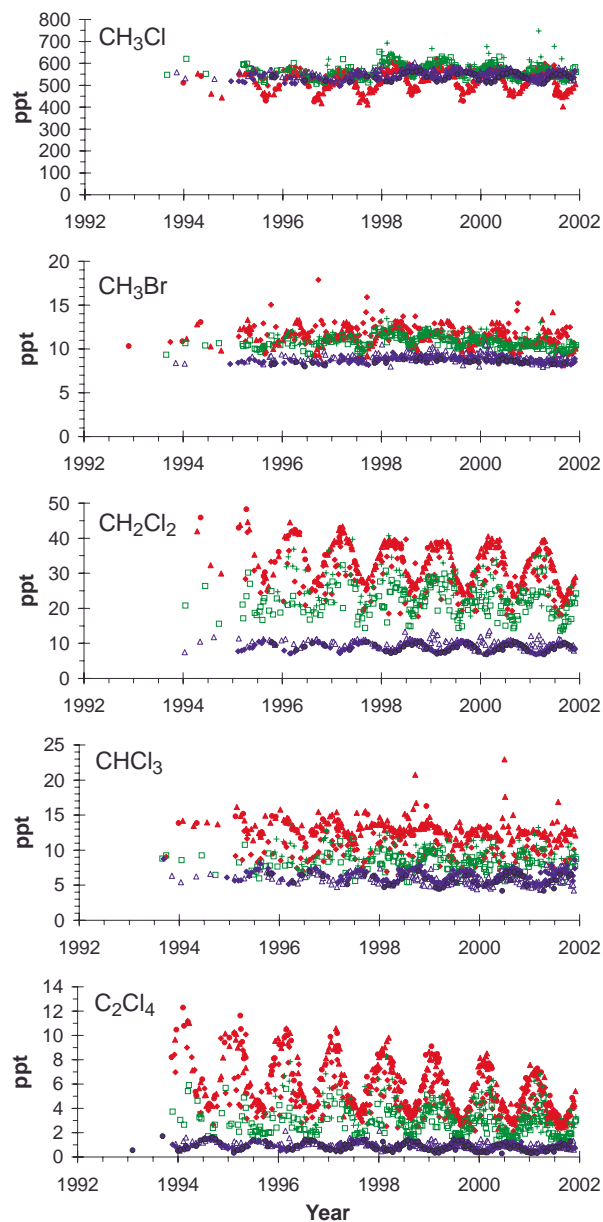


Fig. 5.13. Atmospheric dry-air mole fractions (ppt) determined for selected chlorinated trace gases and CH_3Br by GC-MSD in the CMDL flask program. Each point represents the mean of two simultaneously filled flasks from one of eight or nine stations (symbols the same as in Figure 5.10). Results shown for all compounds except C_2Cl_4 are from 2.4-L stainless-steel flasks only.

Carbonyl sulfide. Measurements of carbonyl sulfide (COS) were begun from flasks during 2000-2001. COS is

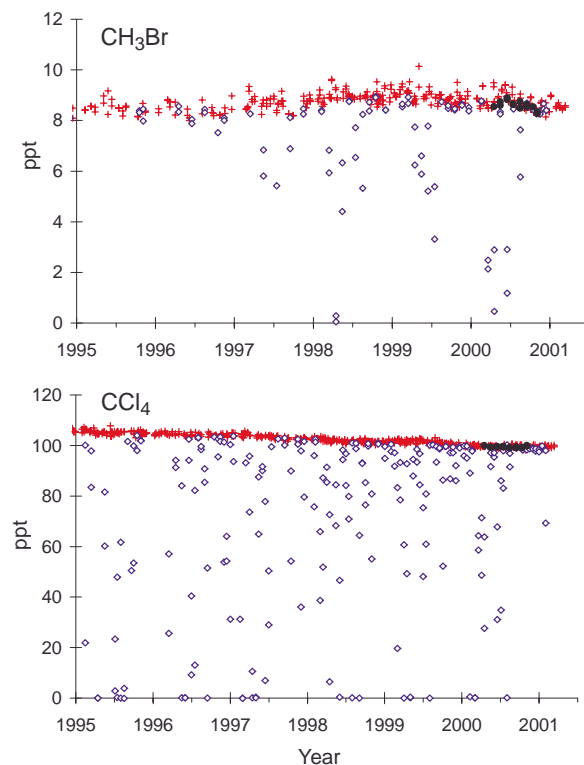


Fig. 5.14. Mixing ratios determined from different sites and different types of flasks. Results for CH_3Br and CCl_4 from Cape Grim, Tasmania (40°S), from stainless-steel flasks (red pluses) are compared with data obtained from South Pole from stainless-steel flasks (open blue diamonds) and glass flasks (solid black circles).

an abundant sulfur-containing gas that is believed to contribute significantly to the sulfur found in the stratosphere. More recent model calculations, however, have suggested a lesser role for COS in maintaining the stratospheric aerosol than was previously thought [Kjellström, 1998].

The results from flasks show a small hemispheric difference biased slightly toward higher levels in the southern hemisphere, strong seasonal variations at all sites except SMO, and seasonality in the two hemispheres that is not 180 days out of phase (Figure 5.15). These features are also evident in data from Chromatograph for Atmospheric Trace Species (CATS) GC-ECD instrumentation located at selected sites. Many conflicting reports regarding hemispheric distributions and seasonality can be found in the current literature for COS. These observations will add substantially to the understanding of the global budget of this gas.

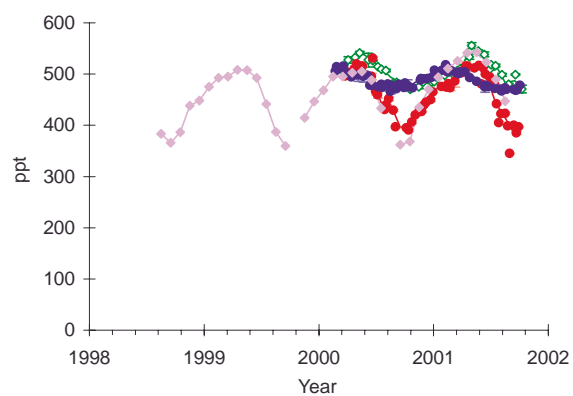


Fig. 5.15. Mixing ratios for COS determined from sampling and analysis of stainless-steel flasks at BRW (red), KUM (green), and CGO (blue). Also shown are monthly means at BRW from the on-site CATS GC-ECD (purple diamonds). For clarity, SMO data are not shown.